

1084175



PATENT SPECIFICATION

NO DRAWINGS

1084175

Date of Application and filing Complete Specification: March 9, 1965.

No. 9994/65.

Application made in Switzerland (No. 3620) on March 20, 1964.

Complete Specification Published: Sept. 20, 1967.

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Index at acceptance:—C2 C(1F1A2, 1F1B, 1F1D3, 1H1A2, 1H1C3, 1J1C3, 1J1E, 1J2C3, 1J2E, 2A3, 2A9, 2A13, 2B3A4, 2B3B, 2B3D, 2B3E, 2B3F, 2B3G4, 2B27, 2B42D, 2B42G, 2B42J2, 2B43D1, 2B43D2, 2B43D3, 2B53D2, 2B53G, 2D43A, 2D43S4, 2R15, 2R16, 2R17, 2R18, 2R20, B4A1, B4C, B4D); C3 P(10C8B, 10C10, 10C20D1, 10C20D3, 10D1A); C3 R(3C11, 21C11, 22C11); C5 D(6B1, 6B2, 6B7, 6B12E, 6B12G1, 6B12G2A, 6B12G2B, 6B12G2C, 6B12G3, 6G12G4, 6B12G6, 6B12N1, 6B12N2, 6B12N3); D1 P(1A4, 1C1A, 1C2B, 1C3A, 1C4, 1D)

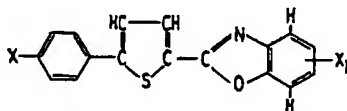
Int. Cl.:—C 07 d 99/02 // C 08 f, g, C 11 d, D 06 l

COMPLETE SPECIFICATION

New Oxazolyl-Thiophene Compounds, process for their preparation and their use

We, CIBA LIMITED, a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides valuable, new oxazolyl-thiophene compounds of the formula



(1) in which one of the symbols X and X₁ represents a hydrogen atom and the other a nitrogen-containing substituent which is a primary, secondary or tertiary amino group, carboxylic acylamino groups, sulphonamido group, urea group or a heterocyclic residue containing nitrogen as part of the heterocyclic ring, said nitrogen-containing substituent being bound to the benzene ring through a trivalent nitrogen atom.

The invention further includes the use of the aforementioned compounds for optically brightening a wide variety of organic materials, as well as a process for optically brightening organic materials with the aid of these compounds.

In the formula (1) the symbol X₁ represents preferably a substituent linked with the benzene nucleus through a trivalent nitrogen atom; as such substituents there are suitable, for example, the amino group —NH₂ and especially the residues of the formulae

(5) —NH—Alk

(6) —NH—CO—Ac

(7) —NH—SO₂—Z

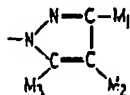
(8) —NH—CO—NH—Z

(9) —NH—Q

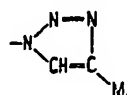
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(11)



(12)

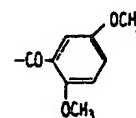
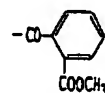
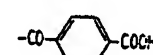
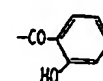
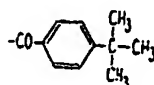
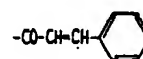
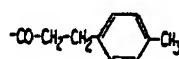
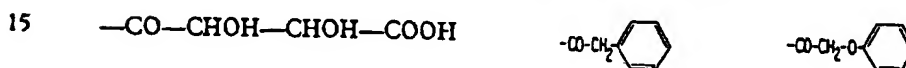
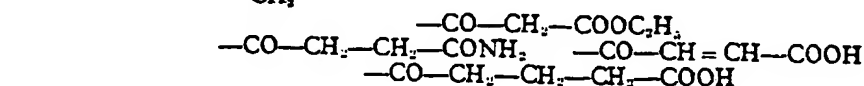
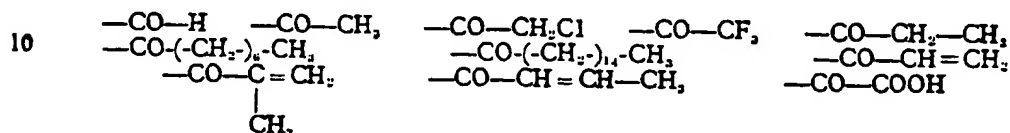


In the formula (5) the symbol Alk represents a possibly substituted alkyl group which advantageously contains at most 4 carbon atoms, e.g. an alkyl group such as methyl, ethyl or n-butyl, or a hydroxyalkyl group such as

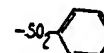
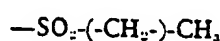
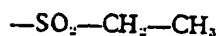
[Price 4s. 6d.]

- 5 or a halogen alkyl group such as $-\text{CH}_2-\text{CH}_2-\text{Cl}$ or $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$, or a cyanoalkyl group such as $-\text{CH}_2-\text{CH}_2-\text{CN}$, or a carboxyalkyl group such as $-\text{CH}_2-\text{COOH}$ or $-\text{CH}_2-\text{CH}_2-\text{COOH}$, or a sulphotoalkyl group such as the $-\text{CH}_2-\text{CH}_2-\text{OSO}_2$ cation.

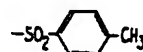
In the formula (6) the symbol $-\text{CO}-\text{Ac}$ represents the acyl radical of an aliphatic, araliphatic or aromatic carboxylic acid. As acyl residues of this kind there may be mentioned, for example:



- 20 The residue $-\text{SO}_2\text{Z}$ in the formula (7) represents the acyl radical of an aliphatic or aromatic sulphonic acid, e.g. a residue of one of the formulae



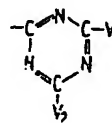
and



- 25 In the formula (8) the symbol Z represents an aliphatic or aromatic residue. Preferred aliphatic residues are the alkyl groups such, for example, as methyl, n-butyl, dodecyl or octadecyl; preferred aromatic residues are those of the benzene series, such as phenyl, para-ethoxyphenyl, para-chlorophenyl, ortho-tolyl and para-tolyl.

As mentioned above, the substituent [X or especially X₁] in the formula (1) which is linked with the benzene ring through a trivalent nitrogen atom, may also correspond to the formula

- 30 (9) $-\text{NH}-\text{Q}$ in which Q represents an s-triazine-2-yl nucleus, for example one of the formula



(13)

in which V₁ and V₂ are identical or different and each represents a halogen atom, espec-

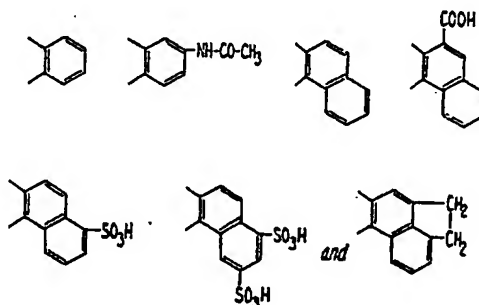
ially chlorine, or a possibly substituted alkoxy, phenoxy, alkylmercapto or phenylmercapto group, or the amino group —NH_2 or the residue of a primary or secondary aliphatic or aromatic amine.

In the formula

(10)



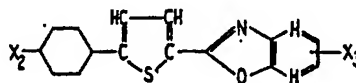
the symbol T represents a benzene residue or especially a naphthalene or acenaphthene residue, e.g.



M_1 , M_2 and M_3 in the above formula (11) are identical or different and each represents a hydrogen atom, an alkyl group containing up to 4 carbon atoms, especially methyl, or a phenyl group, and M_4 in the formula (12) represents a hydrogen atom, an unsubstituted or substituted alkyl group containing up to 4 carbon atoms, such as methyl or hydroxymethyl, or a phenyl group.

The new oxazolyl-thiophene compounds of the formula (1) can be prepared by reducing the nitro group in a compound of the formula

(14)



(in which one of the symbols X_2 , X_3 stands for a hydrogen atom and the other for a nitro group) in known manner to the amino group and, if desired, converting this amino group, likewise in the known manner, substituted nitrogenous groups bound to one of the benzene rings through a trivalent nitrogen atom.

Thus, for example, alkylation, hydroxyalkylation, halogenalkylation or cyanoalkylation of the amino group gives rise to compounds of the formula (1) in which X or X_1 represents a residue of the formula (5).

Furthermore, oxazolyl-thiophene compounds containing a residue of one of the formulae (6) to (9) are accessible by reaction of the appropriate amino compounds with, for example, an acid chloride of an aliphatic, araliphatic or aromatic carboxylic acid, or with an aliphatic or aromatic sulphonylchloride, or with an isocyanate or with a halogeno-1,3,5-triazine.

Oxazolyl-thiophene compounds of the formula (1) — in which one of the symbols X, X_1 represents a hydrogen atom and other a residue of the formula (10)

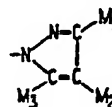


(where T stands for a benzene residue or preferably a naphthalene or acenaphthene residue) are accessible in known manner by diazotization of a suitable amino compound, coupling of the diazo compound so formed with a primary amine of the benzene, naphthalene or acenaphthene series which is capable of coupling in vicinal position to the

amino group, and oxidation of the resulting ortho-aminoazo compound leading to the triazole.

Compounds of the formula (1) that contain as substituent X or X₁ a pyrazole residue of the formula

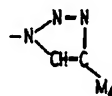
(11)



— in which M₁, M₂ and M₃ have the meanings defined above — are accessible in the known manner, e.g. by converting the free amino group of the oxazolyl-thiophene compound into the hydrazino group and condensation with appropriate α,γ-dicarbonyl compound or the appropriate 3-ketoacetal, to form the pyrazole derivative.

The oxazolyl-thiophene compounds of the formula (1) in which one of the symbols X, X₁ represents a hydrogen atom and the other a triazole residue of the formula

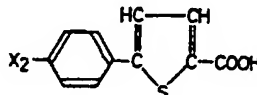
(12)



— where M₄ has the above meaning — can be manufactured, for example, by converting the amino group in a compound of the formula (1) — where X or X₁ stands for the amino group —NH₂— in the known manner into the azido group, the azide then being reacted with acetylene or a suitable acetylene derivative to form the triazole derivative.

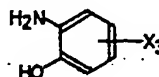
The nitro compounds of the formula (14) to be used as starting materials in the process described above are new; they can be prepared by known methods, for example by reacting a monocarboxylic acid of the formula

(15)



or a functional derivative of such a monocarboxylic acid, at an elevated temperature and preferably in the presence of a catalyst, with an ortho-aminophenol of the formula

(16)



one of the symbols X₂, X₃ in the formulae (15) and (16) representing a hydrogen atom and the other the nitro group.

The monocarboxylic acids of the formula (15) are either known or they can be prepared by known methods (see Journ.org.Chem.21, pages 39 to 44 [1956]). As functional derivatives of the monocarboxylic acids of the formula (15) there may be used, for example, esters with lower aliphatic alcohols, e.g. the methyl or ethyl ester, or especially the acid chlorides.

It is advantageous to react the two components — namely the ortho-aminophenol of the above formula (16) and the monocarboxylic acid of the formula (15) or its functional derivative in at least approximately stoichiometric proportions, that is to say equal or substantially equal molecular proportions of the monocarboxylic acid and of

the aminophenol. The reaction of the two components is carried out by heating at an elevated temperature, for example at about 90 to 260°C, if desired or required in an inert gas, for example in a current of nitrogen. The reaction is advantageously performed in the presence of a catalyst. Suitable catalysts are, for example, boric acid, sulphonic acids of the benzene series such as para-toluenesulphonic acid, also polyphosphoric acids including pyrophosphoric acid, and zinc chloride. The reaction is advantageously carried out so that nitro compounds of the formula (14) are formed directly, that is to say so that the acylation of the ortho-aminophenol and the cyclization to form the oxazole ring take place in a single operational stage.

When boric acid is used as catalyst, it is advantageously employed in an amount of about 0.5 to 5%, referred to the weight of the reaction mixture as a whole. It is also possible to use additionally inert organic high-boiling solvents, for example substitution products of benzene such as ortho-dichlorobenzene, a trichlorobenzene or at most hydrocarbons of the benzene series such as xylene or para-cymene or, especially, high-boiling polar organic solvents such, for example, as dimethylformamide; or aliphatic, possibly etherified, hydroxy compounds, e.g. propyleneglycol, ethyleneglycol monoethyl ether or diethyleneglycol diethyl ether. The nitro compounds of the general formula (14) are also obtained by simply fusing together the two starting materials in a melt of zinc chloride or in the presence of boric acid.

The new oxazolyl-thiophene compounds of this invention possess in general in the dissolved or finely dispersed state a more or less pronounced fluorescence and are suitable for optically brightening a wide variety of organic materials. Good results are obtained, for example, in brightening acrylic resin lacquers, alkyd resin lacquers, cellulose ester lacquers, e.g. acetylcellulose lacquers or nitrocellulose ester lacquers, also in optically brightening natural fibres such as cotton or wool; or synthetic fibres, e.g. those of cellulose esters such as cellulose propionate or acetylcellulose (cellulose diacetate of cellulose triacetate; acetate rayon), polyamides (e.g. Nylon), polyesters (e.g. "Dacron" or "Terylene"—"Dacron" and "Terylene" are both registered Trade Marks) or of polyolefines such as polyethylene or polypropylene, polyvinylchloride or polyvinylidenechloride, and films, foils, tapes or shaped products made from these synthetic materials or other materials such as polystyrene, polyvinyl alcohol or polyvinyl esters of organic acids, e.g. polyvinyl acetate.

If the present process is to be used for optically brightening fibres — which may be in the form of staple fibres or filaments, in the crude state or in the form of hanks or woven fabrics — it is advantageously carried out in an aqueous medium in which the components concerned are suspended or dissolved. If desired, the treating liquors may further contain a dispersant, for example soaps, polyglycol ethers of fatty alcohols, fatty amines or alkylphenols, cellulose sulphite waste liquor or condensation products of formaldehyde with (possibly alkylated) naphthalenesulphonic acids. It has been found to be especially advantageous to work in a neutral, weakly alkaline or acid bath. Likewise, it is advantageous to perform the treatment at an elevated temperature from about 50 to 100°C, for example at the boiling temperature of the bath or near it (at about 90°C). The improvement according to this invention can also be achieved with solutions in organic solvents.

The new oxazolyl-thiophene derivatives of the formula (2) to be used in the present process may also be added to, or incorporated with, the materials before or during their shaping. Thus, they may be added to the moulding compositions used for the manufacture of films, foils, tapes or shaped articles, or they may be dissolved or finely dispersed in the spinning mass before spinning. The new brighteners may also be added to the reaction mixtures before or during the polycondensation leading, for example, to polyamides or polyesters, or before or during the polymerization of monomers, for example vinyl acetate, to the polymerization masses.

The proportion of the new thiophene derivatives of the formula (2) to be used, referred to the weight of the material to be optically brightened, may vary within wide limits. Even a very small amount, in certain cases for instance as little as 0.01%, may produce a distinct and durable effect. It is, however, also possible to use an amount of up to about 2%.

The new oxazolyl-thiophene derivatives of the formula (2) may also be used as brighteners as follows:

(a) In admixture with dyestuffs or pigments or as additives to dye baths, or printing, discharge or resist pastes. Furthermore also for after-treating dycings, prints or discharge effects.

(b) In admixture with chemical bleaches or as additives to bleaching baths.

(c) In admixture with dressing agents such as starch or synthetic dressings. The products of this invention may also be used, for example, to produce a crease-resistant finish by adding them to the liquors used for this purpose.

(d) In combination with detergents. The detergents and brighteners may be added to the washing liquors separately. It is also of advantage to use detergents that as such contain the brightener. Suitable detergents are, for example, soaps or salts of sulphonated benzimidazoles substituted on the 2-carbon atom by higher alkyl radicals; also salts of monocarboxylic acid esters of the 4 - sulphophthalic acid with higher fatty alcohols; also salts of fatty alcohol sulphonates, alkylarylsulphonic acids or condensation products of higher fatty acids with aliphatic hydroxy-sulphonic or amino-sulphonic acids. Furthermore, there may be used nonionic detergents, for example polyglycol ethers derived from ethylene oxide and higher fatty alcohols, alkylphenols or fatty amines.

If the present process is combined with other treatment or improving operations, the combined treatment is advantageously carried out with the aid of suitable preparations. These stable preparations contain new compounds of the above formula (2) as well as dispersants, detergents, dyestuffs, pigments or dressing agents.

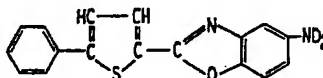
The new compounds of the above formula (2) may also be used after having been fixed on a finely dispersed vehicle.

Parts and percentages in the following Examples are by weight unless otherwise indicated.

EXAMPLE 1

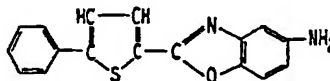
20 parts of the compound of the formula

(17)



are dissolved in 500 parts by volume of dioxane reflux and hydrogenated at 60°C in the presence of 2.5 parts of Raney nickel with hydrogen under atmospheric pressure. When the theoretical amount of hydrogen has been absorbed (after 4½ hours), the reaction mixture is filtered through "Celite" ("Celite" is a Registered Trade Mark) and the filtrate is evaporated to dryness under vacuum, to yield about 17 parts (= 93.5% of the theoretical yield) of the compound of the formula

(18)



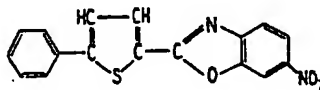
in the form of a light-yellow powder melting at 163 to 165°C. After two recrystallizations from methanol + methylenechloride with the aid of active carbon and diatomaceous earth there are obtained very fine, light-yellow needles melting at 166 to 167°C. Analysis: $C_{17}H_{12}N_2OS$.

mol.weight: 292.36

	C	H	N	S
calculated:	69.84	4.14	9.58	10.97%
found:	69.98	4.06	9.69	11.00%

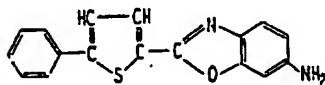
In an analogous manner the compound of the formula

(19)



furnishes the amino compound of the formula

(20)



in a yield of 92% of the theoretical, in light-yellow, small needles from methanol + methylenechloride, melting at 198 to 199°C.

Analysis: $C_{17}H_{12}N_2OS$

5		C	H	N	S	5
	mol.weight: 292.36					
	calculated:	69.84	4.14	9.58	10.97%	
	found:	69.80	4.34	9.59	10.76%	

10 The compound of the formula (17), used as starting material, can be prepared in the following manner: 10

A mixture of 22.3 parts of 5 - phenylthiophene - 2 - carboxylic acid chloride, 15.4 parts of 2 - amino - 4 - nitrophenol, 0.5 part of pyridine and 200 parts by volume of ortho-dichlorobenzene is stirred under nitrogen.

15 The reaction mixture is then raised to the reflux temperature, whereby hydrochloric acid is liberated. When hydrochloric acid is no longer being given off, 1 part of boric acid anhydride is added and the batch is heated within 1 hour to 175 to 180°C, during which water escapes, and then stirred on for about one hour at this temperature. In the course of 1 to 1½ hours the temperature of the reaction mixture is raised to 230 to 240°C, so that the bulk of the solvent distills off drop by drop. The initially yellowish suspension is gradually transformed into a brown melt which is then stirred on for about 60 minutes at 240 to 250°C. 20

25 After having allowed the batch to cool to about 150°C, 200 parts of dioxane are dropped in, whereupon a brown solution forms. After one recrystallization from aqueous dioxane with the aid of active carbon and diatomaceous earth there are obtained about 20 parts (= 62.1% of theory) of the compound of the formula (17) in the form of a light-yellow powder which melts at 220 to 222°C. After two further recrystallizations from dioxane there are obtained very fine, light-yellow needles melting at 227 to 228°C.

Analysis: $C_{17}H_{10}O_2N_2S$

30		C	H	N	S	30
	mol.weight: 322.34					
	calculated:	63.34	3.13	8.69	9.95%	
	found:	63.26	2.98	8.70	10.03%	

35 In an analogous manner the reaction of 5 - phenylthiophene - 2 - carboxylic acid chloride with 2 - amino - 5 - nitrophenol furnishes the nitro compound of the formula (19), in a yield of 73.4%, in light-yellow, small needles from dioxane, melting at 196 to 197°C. 35

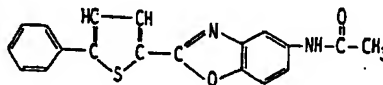
Analysis: $C_{17}H_{10}O_2N_2S$

40		C	H	N		40
	mol.weight: 322.34					
	calculated:	63.34	3.13	8.69%		
	found:	63.61	3.27	8.38%		

EXAMPLE 2

45 57 Parts of the nitro compound of the formula (17) are stirred in 500 parts of glacial acetic acid under reflux. In the course of 2 hours, 50 parts of zinc dust are then added and the reaction mixture is stirred on for 3 hours under reflux. The hot, yellowish brown reaction solution is suction-filtered and the zinc dust washed with 100 parts of hot glacial acetic acid on the suction filter. The filtrate is concentrated under vacuum to about 150 parts and then stirred into 2000 parts of cold water. The precipitated reaction product is suctioned off, washed with cold and then with hot water and dried. There are obtained about 48 parts (= 93% of theory) of the compound of the formula 50

(21)



in the form of a brown powder. After three recrystallizations from chlorobenzene with the aid of active carbon and diatomaceous earth there are obtained very fine, light-yellow needles melting at 215 to 216°C which display a strong blue fluorescence in ultraviolet light.

5 Analysis: $C_{19}H_{14}N_2O_2S$

mol.weight: 334.39

C H N

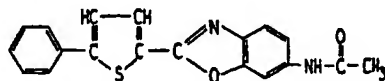
calculated: 68.24 4.22 8.38%

found: 68.31 4.17 8.18%

10 The identical compound is obtained when the compound of the formula (18) is acylated with acetic anhydride + + pyridine.

In an analogous manner the compound of the formula (19) furnishes the acetyl compound of the formula

(22)



15 in a yield of 90% of theory, in light-yellow needles from chlorobenzene, melting at 253 to 254°C.

Analysis: $C_{19}H_{14}N_2O_2S$

Mol.weight: 334.39

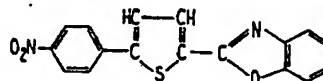
C H N

calculated: 68.24 4.22 8.38%

found: 68.17 4.19 8.37%

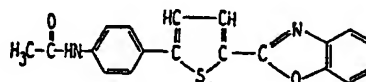
In an analogous manner the compound of the formula

(23)



(obtained by condensing 5 - para - nitrophenyl - thiophene - 2 - carboxylic acid with ortho - aminophenol; melting at 230 to 232°C) furnishes the acetyl compound of the formula

(24)



in a yield of 95% of the theoretical, in small, yellow needles from aqueous dioxane, melting at 219 to 220°C.

Analysis: $C_{19}H_{14}N_2O_2S$

mol.weight: 334.39

C H N

calculated: 68.24 4.22 8.38%

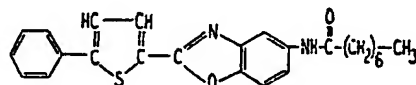
found: 68.02 4.21 8.44%

EXAMPLE 3

11.7 parts of caprylchloride are added to a mixture of 7 parts of the compound of the formula (21) and 50 parts by volume of pyridine. The mixture is refluxed for 2 hours and then evaporated to dryness under vacuum.

After one recrystallization from chlorobenzene with the aid of active carbon and diatomaceous earth there are obtained about 5 parts (= 49.3% of the theoretical yield) of the compound of the formula

(25)



which, after two further recrystallizations from chlorobenzene, forms very fine white crystals melting at 181 to 182°C, which display a strong blue fluorescence in ultra-violet light.

5 Analysis: $C_{25}H_{26}N_2O_2S$
Mol. weight: 418.56

5

	C	H	N
calculated:	71.74	6.26	6.69%
found:	71.71	6.13	6.75%

EXAMPLE 4

10

10 The compounds listed in the following Table I are obtained by the following general method:

15 0.3 Mol of the carboxylic acid chloride concerned is added to a solution of 0.1 mol of the compound of the formula (21) in 150 parts by volume of pyridine, the whole is refluxed for 2 hours and then evaporated to dryness under vacuum. The resulting acylamino compound is recrystallized from the solvent shown in the Table.

15

(26)

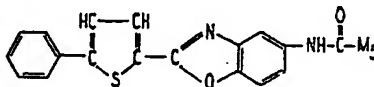
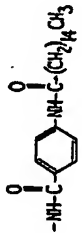
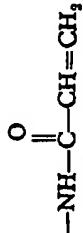
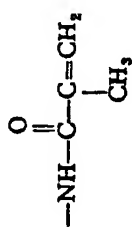
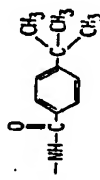


TABLE I

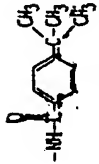
No.	-NH.CO.M ₃ =	Properties	Analysis	
			calculated	found
27		white crystals from chloro- benzene m.p. 218 to 219°C.	C 73.93 H 7.29 N 6.47 C ₁₆ H ₁₄ O ₃ N ₃ S	C 74.46 H 7.68 N 5.74
28		yellowish crystals from chloro- benzene m.p. 219 to 220°C.	C 69.35 H 4.07 N 8.09 C ₂₀ H ₁₄ O ₃ N ₃ S	C 68.91 H 4.06 N 8.11
29		yellowish crystals from chloro- benzene m.p. 215 to 216°C.	C 69.98 H 4.47 N 7.77 C ₂₁ H ₁₆ O ₃ N ₃ S	C 69.74 H 4.45 N 7.58
30		yellowish crystals from aqueous dioxane m.p. 257 to 258°C.	C 74.31 H 5.35 N 6.19 C ₂₈ H ₂₄ N ₂ O ₃ S	C 74.05 H 5.28 N 6.45

In an analogous manner the reaction of the compound of the formula (22) with the corresponding carboxylic acid chlorides furnishes the acylamino compounds shown in the following Table II:

(31)



TABLE II

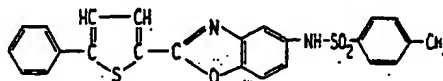
No.	—NH.CO.M _n =	Properties	Analysis	
			calculated	found
32	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—NH—C—(CH}_2\text{)}_6\text{—CH}_3 \end{array}$	white crystals from chlorobenzene m.p. 209 to 210°C.	C 71.74 H 6.26 N 6.69	C 71.47 H 5.82 N 6.85
			C ₂₃ H ₁₈ N ₂ O ₃ S	
33	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—NH—C—(CH}_2\text{)}_{11}\text{—CH}_3 \end{array}$	white crystals from dioxane m.p. 187 to 188°C.	C 74.68 H 7.98 N 5.28	C 74.93 H 7.82 N 5.17
			C ₃₃ H ₄₂ N ₂ O ₃ S	
34		yellowish crystals from dioxane m.p. 266 to 256°C.	C 74.31 H 5.35 N 6.19	C 74.23 H 5.27 N 6.37
			C ₂₈ H ₁₈ N ₂ O ₃ S	
35	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—NH—C—CH=CH}_2 \end{array}$	yellowish crystals from chlorobenzene m.p. 232 to 233°C.	C 69.35 H 4.07 N 8.09	C 69.31 H 3.99 N 8.17
			C ₂₀ H ₁₄ O ₂ N ₂ S	
36	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—NH—C—CH}_2\text{—CH}_2\text{—Br} \end{array}$	light-yellow crystals from dioxane m.p. 237 to 239°C.	C 56.21 H 3.54 N 6.56	C 56.47 H 3.76 N 6.67
			C ₂₀ H ₁₆ N ₂ O ₂ SBr	

EXAMPLE 5

3.26 Parts of para-toluenesulphonylchloride are added to a mixture of 5 parts of the compound of the formula (18) and 50 parts of volume of pyridine. The mixture is refluxed for 2 hours and then evaporated to dryness under vacuum.

After one recrystallization from ethylenechloride + ethanol with the acid of active carbon and diatomaceous earth there are obtained about 6.2 parts (= 81% of theory) of the compound of the formula

(37)



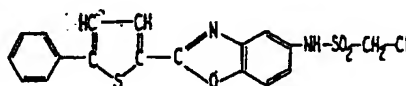
which, after another two recrystallizations from ethylenechloride + ethanol, forms very fine, light-yellow crystals melting at 211 to 212°C which display a strong blue fluorescence in ultraviolet light.

Analysis: $C_{24}H_{18}N_2S_2O_3$
mol.weight: 446.53

	C	H	N	S
calculated:	64.55	4.06	6.27	14.36%
found:	64.66	4.11	6.27	14.45%

In an analogous manner the compound of the formula (18) furnishes the sulphonamide of the formula

(38)



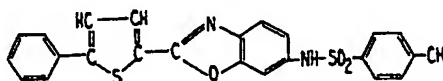
in a yield of 57% of the theoretical, in light-yellow needles from methanol + ethylenechloride, melting at 215 to 216°C.

Analysis: $C_{18}H_{12}O_2N_2ClS_2$
mol.weight: 404.88

	C	H	N	Cl
calculated:	53.50	3.25	6.92	8.79%
found:	53.69	3.29	6.75	9.48%

In an analogous manner the compound of the formula (20) furnishes the sulphonamide of the formula

(39)



in a yield of 76% of the theoretical, in light-yellow needles from methanol + methylenechloride, melting at 219 to 212°C.

Analysis: $C_{24}H_{18}N_2S_2O_3$
mol.weight: 446.53

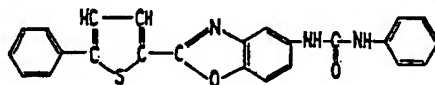
	C	H	N	S
calculated:	64.55	4.06	6.27	14.36%
found:	64.65	4.10	6.24	14.48%

EXAMPLE 6

1.64 Parts of phenylisocyanate are added to a mixture of 4 parts of the compound of the formula (18) and 100 parts by volume of chlorobenzene. The reaction mixture is refluxed for one hour then evaporated to dryness under vacuum.

After one recrystallization from dimethylformamide + ethanol with the aid of active carbon and diatomaceous earth there are obtained about 4.5 parts (= 79.5% of theory) of the compound of the formula

(40)



which, after two further recrystallizations from dimethylformamide + ethanol, forms very fine, light-yellow crystals melting above 300°C.

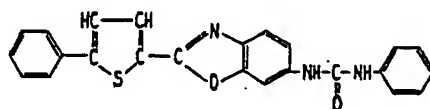
Analysis: $C_{24}H_{11}O_2N_3S$

mol. weight: 411.47

	C	H	N	S
calculated:	70.05	4.16	10.21	7.79%
found:	69.79	4.15	10.14	8.07%

In an analogous manner the compound of the formula (20) furnishes the compound of the formula

(41)



in a yield of 71% of the theoretical, in light-yellow needles from dimethylformamide + ethanol, melting above 300°C.

Analysis: $C_{24}H_{11}O_2N_3S$

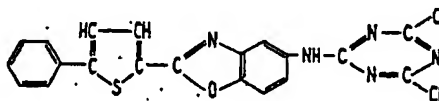
mol. weight: 411.47

	C	H	N	S
calculated:	70.05	4.16	10.21	7.79%
found:	70.02	4.06	10.70	8.09%

EXAMPLE 7

A solution of 3.68 parts of cyanuric chloride in 100 parts by volume of acetone is tipped into a vigorously stirred mixture of 50 parts of ice and 50 parts by volume of water. The resulting cyanuric chloride suspension is cooled to 0 to 5°C, and at this temperature a solution of 5.85 parts of the amino compound of the formula (18) in 200 parts by volume of acetone and an N-sodium hydroxide solution are simultaneously dropped in at such a rate that the pH value remains constant between 6 and 7. The reaction mixture is stirred on for one hour, suction-filtered and the filter cake is washed neutral with water and then dried at room temperature under vacuum, to yield 7 parts (= 78.5% of theory) of the compound of the formula

(42)



in the form of a light-yellow powder which melts at 217 to 219°C. After three recrystallizations from chlorobenzene with the aid of active carbon it forms very fine, light-yellow needles melting at 249 to 250°C.

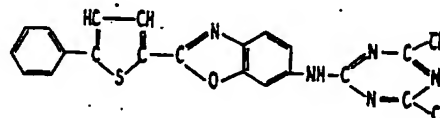
Analysis: $C_{26}H_{11}N_5Cl_2SO$

Mol. weight: 440.31

	C	H	N	Cl	S
calculated:	54.56	2.52	15.91	16.10	7.28%
found:	54.91	2.80	16.22	15.48	7.51%

In an analogous manner the compound of the formula (20) furnishes the compound of the formula

(43)



in a yield of 94.5% of the theoretical, in small, light-yellow needles from chlorobenzene, melting at 255 to 256°C.

Analysis: $C_{20}H_{11}N_5Cl_2SO$

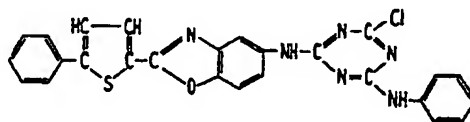
Mol. weight: 440.31

	C	H	N	Cl	S
calculated:	54.56	2.52	15.91	16.10	7.28%
found:	54.79	2.79	15.90	15.98	7.30%

EXAMPLE 8

4.4 Parts of the compound of the formula (42) are dissolved in 100 parts by volume of anhydrous dioxane by heating to 80°C. The resulting clear solution is cooled to 30°C, and at this temperature a solution of 1.02 parts of aniline in 25 parts by volume of dioxane and an N-sodium hydroxide solution are simultaneously dropped in at such a rate that the pH value remains constant between 6 and 7. The reaction mixture is stirred on for one hour at 49°C, suction-filtered and the filter cake is washed neutral with water and then dried at 50°C under vacuum, to yield 4.5 parts (= 92% of theory) of the compound of the formula

(44)



in the form of a light-yellow powder which melts at 225 to 227°C. After three recrystallizations from chlorobenzene with a aid of active carbon it forms very fine, light-yellow crystals melting at 234 to 235°C.

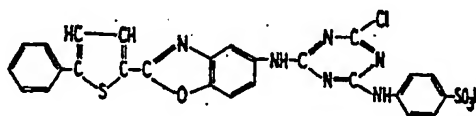
Analysis: $S_{20}H_{11}ON_5ClS$

mol. weight: 496.96

	C	H	N	Cl	S
calculated:	62.84	3.45	16.91	7.13	6.45
found:	62.50	3.87	15.88	7.04	6.18

In an analogous manner the reaction of the compound of the formula (42) with sulphanilic acid furnishes the compound of the formula

(45)

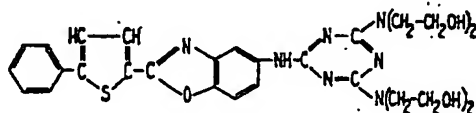


in a yield of 71% of the theoretical, as a yellow powder melting at 293 to 295°C with decomposition

EXAMPLE 9

A mixture of 7.5 parts of the compound of the formula (42) and 25 parts by volume of diethanolamine is refluxed for $\frac{1}{2}$ hour. The reaction mixture is then cooled to room temperature and poured into water, to yield about 5.2 parts (= 52.5% of theory) of the compound of the formula

(46)



in the form of a light-yellow powder which melts at 184 to 185°C. After three crystallizations from ethanol with the aid of active carbon and diatomaceous earth it forms very fine, light-yellow needles melting at 196 to 198°C.

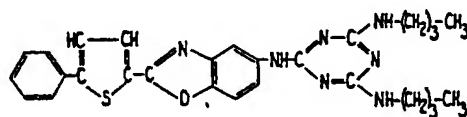
Analysis: $C_{28}H_{31}N_7O_3S$

mol. weight: 577.64

	C	H	N	S
calculated:	58.22	5.41	16.97	5.55
found:	57.36	5.40	16.94	5.73

In an analogous manner the reaction of the compound of the formula (42) with butylamine furnishes the compound of the formula

(47)



in a yield of 65% of the theoretical, in small, light-yellow needles from aqueous dioxane, melting at 177 to 178°C.

Analysis: $C_{28}H_{31}N_7OS$

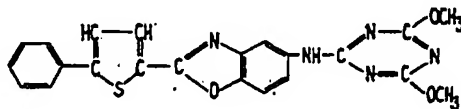
mol. weight: 513.65

	C	H	N
calculated:	65.47	6.08	19.09
found:	65.78	6.17	19.18

EXAMPLE 10

A mixture of 5.84 parts of the compound of the formula (18), 3.86 parts of 2-chloro - 4,6 - dimethoxy - s - triazine, 1.86 parts of sodium bicarbonate and 150 parts by volume of methylcellosolve is stirred for 2 hours at 100°C, then cooled to room temperature and suction-filtered, to yield 7.3 parts (= 85% of theory) of the compound of the formula

(48)



in the form of a yellow powder melting at 227°C with decomposition, which after three recrystallizations from chlorobenzene with the aid of active carbon and diatomaceous earth forms very fine crystals melting at 235 to 236°C.

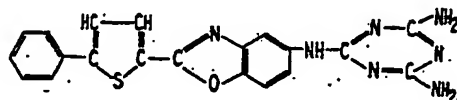
Analysis: $C_{28}H_{31}N_7O_5S$

mol. weight: 431.46

	C	H	N	S
calculated:	61.34	3.97	16.23	7.43
found:	60.94	4.02	16.25	7.57

In an analogous manner the reaction of the compound of the formula (18) with 2-chloro - 4,6 - diamino - s - triazine furnishes the compound of the formula

(49)



in a yield of 87.5% of the theoretical, in light-yellow crystals from dioxane, melting at 271 to 272°C.

Analysis: $C_{22}H_{13}N_3OS$

mol. weight: 401.49

	C	H	N	S
calculated:	59.84	3.77	24.42	7.99
found:	59.89	3.75	23.57	7.94

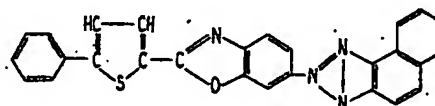
EXAMPLE 11

20 Parts by volume of concentrated hydrochloric acid and 80 parts by volume of water are stirred into a suspension of 14.6 parts of the amino compound of the formula (20) in 250 parts by volume of glacial acetic acid. A solution of 2.5 parts of sodium nitrate in 20 parts by volume of water is slowly added dropwise with vigorous stirring at 0 to 5°C into the resulting yellow suspension. The reaction mixture is stirred on for 4 hours at 50°C and then suction-filtered. The resulting clear diazonium solution is slowly mixed with a 2% solution of sulphamic acid until the excess of sodium nitrite has been decomposed.

The diazonium solution is cooled to 5°C and at this temperature, within 15 minutes, a hot solution of 7.5 parts of α -naphthylamine in 100 parts by volume of water and 10 parts by volume of concentrated hydrochloric acid is dropped in. The reaction mixture is stirred on for 2 hours at 10°C, mixed with a solution of 40 parts of sodium acetate in 100 parts by volume of water and then stirred on for 16 hours at room temperature. The resulting dyestuff is suctioned off and washed with 500 parts by volume of water.

The filter cake is suspended in 400 parts by volume of picoline and heated to 95°C. A solution of 36 parts of copper sulphate in 100 parts by volume of water is slowly dropped in. The reaction mixture is stirred on overnight at 25°C, then cooled to room temperature, and suction-filtered, to yield about 12 parts (= 47.5% of theory) of the compound of the formula

(50)



in the form of a yellow powder which melts at 264 to 267°C. After two recrystallizations from chlorobenzene with the aid of active carbon and diatomaceous earth it forms small, very fine needles melting at 266 to 267°C.

Analysis: $C_{27}H_{14}N_3OS$

mol. weight: 444.49

	C	H	N
calculated:	72.96	3.63	12.60
found:	72.92	3.77	12.48

EXAMPLE 12

Bleached cotton fabric is treated at a goods-to-liquor ratio of 1 : 30 for half an hour at 20 to 50°C in a bath containing (referred to the weight of the textile material treated) 1.5% of the compound of the formula (21) or (22) or of a mixture of these two compounds and 5g of crystalline sodium sulphate per litre.

After having been rinsed and dried, the cotton fabric treated in this manner has a higher white content than the untreated starting fabric.

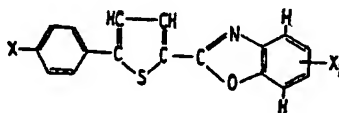
EXAMPLE 13

An intimate mixture of 100 parts of polyvinylchloride, 54 parts of dioctylphthalate, 2 parts of titanium dioxide and 0.1 part of one of the compounds (28), (29), (32), (33) or (35) is rolled on a calender for 6 minutes at 150 to 160°C to form a film.

The film manufactured in this manner has a very high white content which displays excellent fastness to light.

WHAT WE CLAIM IS:

1. Oxazoly-thiophene compounds of the formula



in which one of the symbols X and X₁ represents a hydrogen atom and the other a nitrogen-containing substituent which is a primary, secondary and tertiary amino group, carboxylic acylamino groups, sulphonamido group, urea group or a heterocyclic residue containing nitrogen as part of the heterocyclic ring, said nitrogen-containing substituent being bound to the benzene ring through a trivalent nitrogen atom.

2. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a residue of the formula —NHAlk, in which Alk stands for an alkyl group of 1—4 carbon atoms which may be substituted.

3. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a residue of the formula —NH—COAC, in which —COAC, stands for the acyl residue of an aliphatic, araliphatic or aromatic carboxylic acid.

4. Compounds as claimed in claim 1 in which the nitrogen-containing substituent is a residue of the formula —NH—SO₂—Z in which —SO₂—Z represents the acyl residue of an aliphatic or aromatic sulphonic acid.

5. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a residue of the formula —NH—CO—NH—Z in which Z represents an aliphatic or aromatic residue.

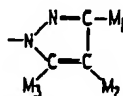
6. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a residue of the formula —NH—Q in which Q represents an s-triazin-2-yl nucleus.

7. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a residue of the formula



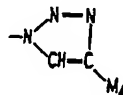
in which T represents a benzene residue or especially a naphthalene or acenaphthene residue.

8. Compounds as claimed in claim 1, in which the nitrogen-containing substituent is a pyrazole residue of the formula



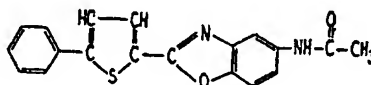
in which M₁, M₂ and M₃ are identical or different and each represents a hydrogen atom, an alkyl group of up to four carbon atoms or a phenyl group.

9. Compounds as claimed in claim 1, in which the nitrogen-containing compound is a triazolyl residue of the formula

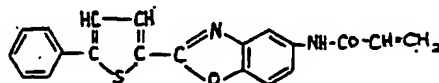


in which M₄ represents a hydrogen atom, an alkyl group (if desired substituted) of up to 4 carbon atoms or a phenyl group.

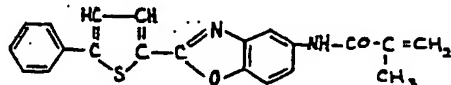
10. The compound of the formula



11. The compound of the formula



12. The compound of the formula



5 13. Oxazolyl-thiophene compounds according to claim 1 substantially as herein- 5
before described.

14. Any of the oxazolyl-thiophene compounds according to claim 1 hereinbefore 10
identified.

15. A process for optically brightening organic materials, which comprises adding 10
to or incorporating in the material to be brightened an oxazolyl-thiophene compound
as claimed in any of claims 1—14.

16. A process as claimed in claim 15, wherein for optically brightening polyconden-
sates or addition polymers the oxazolyl-thiophene compound is added to the starting 15
materials before or during the polycondensation or polymerization respectively.

17. Brightening preparations containing at least one new oxazolyl-thiophene com- 15
pound as claimed in any one of claims 1 to 14, and one or more dispersants, carriers,
detergents, dyestuffs, pigments or dressing agents.

18. Any organic material that has been optically brightened by a process as claimed 20
in claims 16 or 17 or by incorporation or addition of a preparation as claimed in claim
17.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,
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